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**SILICON NITRIDE POWDER**

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**Abstract**

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**PURPOSE:** To provide a silicon nitride powder capable of providing a silicon nitride sintered compact having high strength, small in the dispersion of strength and dimension and high in reliability.

**CONSTITUTION:** The dispersibility of the silicon nitride powder is drastically improved in a mixed solvent by making the silicon nitride powder  $\geq 0.2 \mu\text{eq./m}^2$  surface acidic group quantity per B.E.T. surface area and by using the silicon nitride powder, a molding having high density and uniform quality is obtained and the silicon nitride sintered compact having high strength, small in the dispersion of strength and dimension and high in reliability is easily formed.

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[Title of the Invention]

## SILICON NITRIDE POWDER

[Abstract]

[Object] To provide a silicon nitride powder capable of providing a silicon nitride sintered body which is high in strength, small in the dispersion of strength and size and high in reliability.

[Constitution] The dispersibility of the silicon nitride powder is drastically improved in a mixed solvent by making the silicon nitride powder having a surface acidic group amount per B.E.T. surface area of  $0.2 \mu\text{eq}/\text{m}^2$  or more and, by using the silicon nitride powder, a formed body having high density and uniform quality is obtained and the silicon nitride sintered body which is high in strength, small in the dispersion of strength and size and high in reliability can be easily formed.

[Claims]

1. A silicon nitride powder having a surface acidic group amount per B.E.T. surface area of  $0.2 \mu\text{eq}/\text{m}^2$  or more.
2. The silicon nitride powder according to Claim 1, wherein an average primary particle diameter is  $0.5 \mu\text{m}$  or less and a surface acidic group amount per B.E.T. surface area is  $1.0 \mu\text{eq}/\text{m}^2$  or more.
3. The silicon nitride powder according to Claim 1, wherein the atomic ratio  $[\text{Si}^*/\text{Si}]$  of silicon  $[\text{Si}^*]$  derived from  $\text{SiO}_2$  to the surface silicon

[Si] obtained by x-ray photospectrometry (XPS) is 0.01 or more.

4. The silicon nitride powder according to Claim 2, wherein the atomic ratio  $[Si^*/Si]$  of silicon  $[Si^*]$  derived from  $SiO_2$  to the surface silicon [Si] obtained by x-ray photospectrometry (XPS) is 0.07 or more.

[Detailed Description of the Invention]

[0001]

[Industrial Field of the Invention]

The invention relates to a silicon nitride powder and, more particularly, to a silicon nitride powder which gives a highly dense and evenly powder-packed formed body necessary to obtain a silicon nitride sintered body which is high in strength, small in the dispersion of strength and size and high in reliability.

[0002]

[Prior Art]

A silicon nitride sintered body is generally produced by mixing a silicon nitride powder with a sintering aid powder of mainly  $Al_2O_3$  or the like in a solvent such as trichloroethane for producing a slurry, mixing a binder for formation with the slurry, and then either directly forming the obtained slurry by casting or pressure-casting method or drying the slurry and forming the dried product by press forming or extrusion forming, and firing the obtained formed body after degreasing the formed body based on the necessity.

[0003]

In such methods, if the sintering conditions such as types, the addition amounts, and the like of sintering aids are the same, the

dispersion of physical properties of sintered bodies, such as the strength, the size precision and the like, are affected mainly by the density and the packed structure of the formed body. Conventionally, with respect to a silicon nitride powder which is to be a raw material powder, in order to increase the density of a formed body, the particle diameter and the particle size distribution are controlled as described in JP Kokai Hei 3-159907. However, the silicon nitride powder to be used as a raw material tends to be made finely granulated in terms of the improvement of the physical properties of a sintered body (for example, Powders and Industries, Tsuneo SHIMAMURA, et. al, P.36, Vol. 21, No. 8 (1989)).

[0004]

[Problems to be Solved by the Invention]

However, in the case of using such a finely granulated silicon nitride powder as a raw material, there occurred problems that the density of an obtained formed body becomes low, that the density of the inside of the formed body becomes uneven, and that pores and voids are formed.

[0005]

Therefore, based on the above-mentioned problems, the present inventors have investigated eagerly and found that the dispersibility of a silicon nitride powder in a solvent in a mixing process is significantly changed depending on the surface properties of the silicon nitride powder and the dispersion state of the silicon nitride powder in the mixing solvent affects the powder-packed structure of the formed body and have accomplished the present invention.

[0006]

Accordingly, an object of the present invention is to provide a silicon nitride powder that can provide a highly dense and evenly powder-packed formed body and give a silicon nitride-based sintered body which is high in strength, small in the dispersion of strength and size and high in reliability.

[0007]

[Means for Solving the Problems]

That is, the present invention is a silicon nitride powder having a surface acidic group amount per B.E.T. surface area of  $0.2 \mu\text{eq}/\text{m}^2$  or more.

[0008]

Use of a silicon nitride powder having a surface acidic group amount per B.E.T. surface area of  $0.2 \mu\text{eq}/\text{m}^2$  or more, preferably  $0.5 \mu\text{eq}/\text{m}^2$  or more, significantly improves the dispersibility of the powder in a solvent and makes it possible to obtain a highly dense and uniform formed body. On the other hand, the dispersion state of a silicon nitride powder having a surface acidic group amount per B.E.T. surface area of less than  $0.2 \mu\text{eq}/\text{m}^2$  in a solvent is considerably deteriorated and agglomeration becomes noticeable.

[0009]

Further, in order to control the micro-structure of a sintered body, a fine silicon nitride powder with  $0.5 \mu\text{m}$  or less of average primary particle diameter is desirably used. In the case of such a fine powder, since the agglomeration force among particles is high, in order to carry

out sufficient dispersion in a solvent, the surface acidic group amount per B.E.T. surface area is preferably  $1.0 \mu\text{eq}/\text{m}^2$  or more.

[0010]

A mixing solvent is not particularly limited; however, the dispersibility in a polar solvent such as an alcohol, water and the like can be remarkably improved by controlling the surface acidic group amount per B.E.T. surface area of a silicon nitride powder to be in the above-mentioned range and the higher the dielectric constant of a solvent becomes, the more such tendency is emphasized.

[0011]

As the solvent, water is excellent since it has a high dielectric constant, is economical and does not require safety measures for explosion prevention unlike a combustible organic solvent; however, stability of silicon nitride to water could be a matter. With respect to such a matter, use of a silicon nitride powder having 0.07 or more atomic ratio  $[\text{Si}^*/\text{Si}]$  of silicon  $[\text{Si}^*]$  derived from  $\text{SiO}_2$  to the surface silicon  $[\text{Si}]$  obtained by x-ray photospectrometry (XPS) is effective to carry out mixing the powder stably in water. Further, the dispersibility can be improved by controlling the surface acidic group amount per B.E.T. surface area to be in the above-mentioned range. In the case of using a silicon nitride powder with less than 0.07 atomic ratio  $[\text{Si}^*/\text{Si}]$ , the silicon nitride is decomposed by water; therefore, it is not preferable.

[0012]

The silicon nitride powder having  $0.2 \mu\text{eq}/\text{m}^2$  or more of surface acidic group amount per B.E.T. surface area can be obtained by heating a

silicon nitride powder synthesized by an imide decomposition method, a direct nitridation method or the like in an atmosphere containing 1% by volume of oxygen or more or an atmosphere containing 0.5% by volume or more steam. The treatment temperature is preferably 500 to 850°C in the case of oxygen-containing atmosphere and 200 to 800°C in the case of steam-containing atmosphere.

[0013]

Since  $\text{SiO}_2$  coating film is formed on the silicon nitride surface by the above-mentioned heating treatment, the ratio  $[\text{Si}^*/\text{Si}]$  in the silicon nitride surface can be made to be 0.07 or more by controlling the treatment duration.

[0014]

At the time of mixing the silicon nitride powder with a sintering aid powder, wet mixing using a variety of solvents is generally carried out. At that time, in order to improve the dispersibility of mainly the sintering aid powder, a surfactant or a deflocculation agent is added. However, even if the dispersibility of the sintering aid powder in a solvent is improved to a far extent, in the case the dispersibility of the silicon nitride powder, which is a main component, in the solvent is insufficient, agglomeration of the silicon nitride powder takes place and especially in wet forming, by a casting formation method or a pressure casting formation method, agglomeration of the silicon nitride powder may be a cause of uneven density of an obtained formed body and of pore and void formation.

[0015]

Further, also in the case of carrying out drying and granulation by a spray drier or the like, pores may be formed and uneven structure is formed during the granulation. Further in the above-mentioned wet formation or drying, the higher the agglomeration force among particles becomes, the more unevenly the particles of the powder are brought into contact with one another with solvent removal, resulting in unevenly and sparsely packed structure and an uneven and low density formed body formation.

[0016]

When shearing force is applied during a step of stirring the silicon nitride powder in the solvent, weakly agglomerated particles are temporarily deflocculated; however, they are soon agglomerated again and, therefore, the dispersibility depends on the equilibrium state between deflocculation and agglomeration.

[0017]

With respect to a polar solvent, electrostatic repulsive force attributed to the electric charge on the powder surface contributes to the dispersibility by suppression of the re-agglomeration and in order to effectively draw the electrostatic repulsive force, it is required to cover the surface of the silicon nitride powder particles with the solvent at first. That is, if the wettability of the silicon nitride powder to the solvent is low, the dispersibility of the silicon nitride powder is poor and the solvent does not penetrate agglomerates formed, not to speak of the immersion in the solvent and the penetration into the particles of the powder forming the agglomerates, and even if shearing force is applied, it is supposed to be



difficult to easily cause deflocculation.

[0018]

Contrarily, since the silicon nitride powder according to the present invention has a sufficient amount of the surface acidic group with high affinity with a polar solvent to wet the entire powder surface with the solvent, the wettability to the solvent is remarkably improved and the dispersibility of the powder in the solvent can be considerably improved.

[0019]

Further, in the case of using water as the polar solvent, silicon nitride is decomposed by water. However when a silicon nitride powder with the above-mentioned atomic ratio  $[Si^*/Si]$  of 0.07 or more is used, decomposition by water can be prevented by  $SiO_2$  coating film existing on the surface of the silicon nitride powder.

[0020]

It is noted that the surface acidic group amount per B.E.T. surface area and the  $[Si^*/Si]$  ratio in the present invention was measured by the following methods.

[0021]

(Surface acidic group amount per B.E.T. surface area)

After a silicon nitride powder was vacuum dried at  $110^\circ C$  for 12 hours, 10 g of the resulting powder was measured, loaded into a flask made of polypropylene, mixed with 100 ml of an aqueous 1/100 N NaOH solution and shaken at  $25^\circ C$  for 4 hours. The resulting powder was subjected to centrifugal separation and precipitated and 25 ml of the supernatant solution was measured and subjected to titration analysis by

using an aqueous 1/100 N HCl solution and phenolphthalein as an indicator. Similarly, a blank test was carried out in a system free from the silicon nitride powder and the surface acidic group amount per B.E.T. surface area was calculated based on the following equation using the titration analysis value of the blank test as a standard value. The measurement was repeated five times for each sample and the average value was used as the measured value.

[0022]

Surface acidic group amount per B.E.T. surface area ( $\mu\text{eq}/\text{m}^2$ ) =

$$\frac{100/25(B - X) \cdot K}{W \cdot S} \times 1000, \text{ wherein}$$

X: Titrated amount of aqueous HCl solution (ml);  
 B: Titrated amount in blank test (ml);  
 K: Normality of aqueous HCl solution (N);  
 W: Weight of silicon nitride powder (g); and  
 S: B.E.T. surface area of silicon nitride powder ( $\text{m}^2/\text{g}$ )

[0023]

( $[\text{Si}^*/\text{Si}]$  ratio)

After a silicon nitride powder was vacuum dried at 110°C for 12 hours, the powder was subjected to degassing treatment in a preliminary chamber for XPS at a room temperature in vacuum of  $10^{-4}$  to  $10^{-5}$  torr for 1 to 8 hours and the resulting sample was introduced into an analysis chamber, measurement was carried out after the vacuum degree in the background was decreased to  $10^{-10}$  torr level. The total silicon [Si] in the surface was measured based on the  $\text{Si}2\text{p}$  peak. Further, the waveform of

the Si<sub>2</sub>p peak was separated and it was assumed that the peak of 103.4 eV  $\pm$  0.5 eV was attributed to [Si\*] derived from the SiO<sub>2</sub> and the [Si\*/Si] ratio by atom was calculated. ESCA 5400 MC manufactured by Perkin Elmer Co. was employed for the measurement and monochrome AlK $\alpha$  was used as the x-ray source.

[0024]

Hereinafter, examples of the present invention will be described; however, the present invention is not limited thereto.

[0025]

[Example 1]

Silicon nitride powders having the characteristics shown in Table 1 were obtained by heating silicon nitride powders with 96.0% of  $\alpha$ -crystallization ratio and 0.2  $\mu$ m of average primary particle diameter in N<sub>2</sub> atmosphere containing 10% by volume of steam or in atmospheric air.

[0026]

Next, 92 parts by weight of each silicon nitride powder was added with 5 parts by weight of Y<sub>2</sub>O<sub>3</sub> with 0.25  $\mu$ m average primary particle diameter and 3 parts by weight of Al<sub>2</sub>O<sub>3</sub> with 0.15  $\mu$ m average primary particle diameter as sintering aids and further added with ethanol in an amount of 70% by weight to the entire powder amount and, after the resulting mixture was mixed at 100 rpm for 48 hours by a ball mill made of nylon, a binder in an amount of 0.5% by weight to the entire powder amount was added and successively mixed for 1 hour. After being vacuum defoamed, the obtained slurry was loaded into a porous die and subjected to pressure casting formation in 30 kg/cm<sup>2</sup> pressure to obtain a

formed body of  $10\text{ cm} \times 10\text{ cm} \times 5.5\text{ mm}^2$ . After the formed body was dried at  $100^\circ\text{C}$  for 12 hours, the density was measured at the points shown in Fig. 1 by a  $\gamma$ -ray measurement device for measuring the density in ultrafine parts. The measurement results and the viscosity of each slurry before formation are shown in Table 2. Further, the bulk density calculated from the weight and the size of each formed body is also shown in the same table.

[0027]

Each formed body after drying was cut and polished into 16 specimens with a size of  $8\text{ mm} \times 48\text{ mm} \times 5.5\text{ mm}^2$ . The specimens were degreased at  $750^\circ\text{C}$  for 3 hours and fired at  $1720^\circ\text{C}$  for 5 hours in  $\text{N}_2$  atmosphere and then subjected to HIP treatment at  $1720^\circ\text{C}$  for 3 hours in  $\text{N}_2$  of 1000 atmospheric pressure.

[0028]

The density of each obtained sintered body was measured by Archimedes' method and, after the thickness was measured, each specimen was processed to be a transverse test piece according to JIS R 1601 and subjected to a four-point bending test. The results are shown in Table 2.

[0029]

From the results in Table 2, in the case of using the silicon nitride powders (C to I) of the present invention, the viscosity of each slurry was found decreased attributed to the improved dispersibility in ethanol as compared with the case of using the powders (A and B) of Comparative Examples, and a formed body with a high density and small

density dispersion was obtained. It was found that the average strength, the Weibull coefficient and the size precision were remarkably improved.

[0030]

[Example 2]

With respect to the silicon nitride powders A to I shown in Table 1, formed bodies similar to those of Example 1 were produced from the powders using water as a solvent in the following steps.

[0031]

92 parts by weight of each silicon nitride powder, 5 parts by weight of  $Y_2O_3$  and 3 parts by weight of  $Al_2O_3$  used in Example 1 were made ready and ion exchanged water, the pH of which was adjusted to 9.5 with ammonia, in an amount of 48% by weight to the total powder amount was added to the silicon nitride powder and mixed at 100 rpm for 12 hours by a ball mill made of nylon and, successively,  $Y_2O_3$  and  $Al_2O_3$  were added to the resulting slurry and mixed for 12 hours and further a binder in an amount of 0.5% by weight to the total powder amount was added and further mixed for 1 hour. When the pH of each obtained slurry was measured, the respective pH values of the slurries of the silicon nitride powders A, B, E and G were found increased to pH 11.2, pH 10.7, pH 11.0 and pH 10.8, respectively and it showed that decomposition of the silicon nitride powders by water took place.

[0032]

After each slurry was subjected to vacuum defoaming and formed bodies and sintered bodies were produced in a similar manner to that of Example 1 and the characteristics of the formed bodies and the sintered

bodies were measured. The results are shown in Table 3.

[0033]

From the results in Table 3, in the case of using the silicon nitride powders (C to I) of the present invention, similarly to the results (in Table 2) of Example 1, formed bodies with high density and small density dispersion were obtained as compared with the case of using the silicon nitride powders (A and B) of Comparative Examples and the sintering properties were also found to be improved.

[0034]

Further, with respect to the silicon nitride powders A, B, E and G with a  $[Si^*/Si]$  ratio of less than 0.07, decomposition by water took place and the characteristics of the formed bodies and the sintered bodies were deteriorated as compared with the characteristics in the case of using ethanol as a solvent (Table 2). However, with respect to silicon nitride powders C, D, F, H and I with a  $[Si^*/Si]$  ratio of 0.07 or more, no decomposition by water took place and the characteristics of the formed bodies and the sintered bodies were found to be improved as compared with the case of using ethanol solvent.

[0035]

[Table 1]

Silicon nitride powder No.	Comparative Example		The present invention						
	A	B	C	D	E	F	G	H	I
Surface acidic group amount per B.E.T. surface area ( $\mu\text{eq}/\text{m}^2$ )	0.03	0.15	0.23	0.62	0.65	1.20	1.23	2.14	2.61
[Si <sup>*</sup> /Si] ratio (atomic ratio)	0.04	0.05	0.07	0.11	0.04	0.20	0.05	0.18	0.17

[0036]

[Table 2]

Silicon nitride powder No.			Comparative Example		The present invention						
			A	B	C	D	E	F	G	H	I
Slurry viscosity (CP)			2650	2400	1330	1000	1030	620	618	585	540
Density of formed body (g/cm <sup>3</sup> )	Density measured by $\gamma$ -ray in ultrafine part	Average density	1.581	1.586	1.620	1.635	1.633	1.668	1.670	1.675	1.679
		Dispersion width	0.036	0.033	0.017	0.015	0.017	0.010	0.009	0.007	0.007
	Bulk body	Density	1.582	1.585	1.620	1.634	1.634	1.668	1.669	1.675	1.678
Characteristics of sintered body	Thickness size (mm)	Average thickness	4.320	4.323	4.359	4.368	4.367	4.401	4.400	4.406	4.410
		Dispersion width	0.125	0.118	0.059	0.053	0.054	0.028	0.030	0.025	0.024
	Strength	Bending strength (kg/mm <sup>2</sup> )	105	107	115	117	116	122	122	124	123
		Weibull coefficient	13	14	18	19	18	21	21	22	22



[0037]

[Table 3]

Silicon nitride powder No.			Comparative Example		The present invention						
					A	B	C	D	E	F	G
Slurry	Viscosity (CP)		5500	4950	2850	2300	2890	1050	2030	250	230
	pH		11.2	10.7	9.7	9.6	11.0	9.5	10.8	9.5	9.5
	Density of formed body (g/cm <sup>3</sup> )	Density measured by γ-ray in ultrafine part	Average density	1.583	1.585	1.698	1.720	1.706	1.807	1.769	1.842
Dispersion width			0.042	0.035	0.014	0.012	0.020	0.009	0.022	0.006	0.007
Bulk body		Density	1.584	1.592	1.696	1.721	1.705	1.808	1.769	1.853	1.856
		Thickness size (mm)	Average thickness	4.322	4.322	4.428	4.462	4.430	4.521	4.490	4.554
Characteristics of sintered body	Strength		Dispersion width	0.134	0.124	0.033	0.031	0.062	0.015	0.058	0.012
		Bending strength (kg/mm <sup>2</sup> )	98	100	120	123	112	126	115	129	128
	Weibull coefficient	12	12	20	20	17	24	18	25	26	

[0038]

[Effects of the Invention]

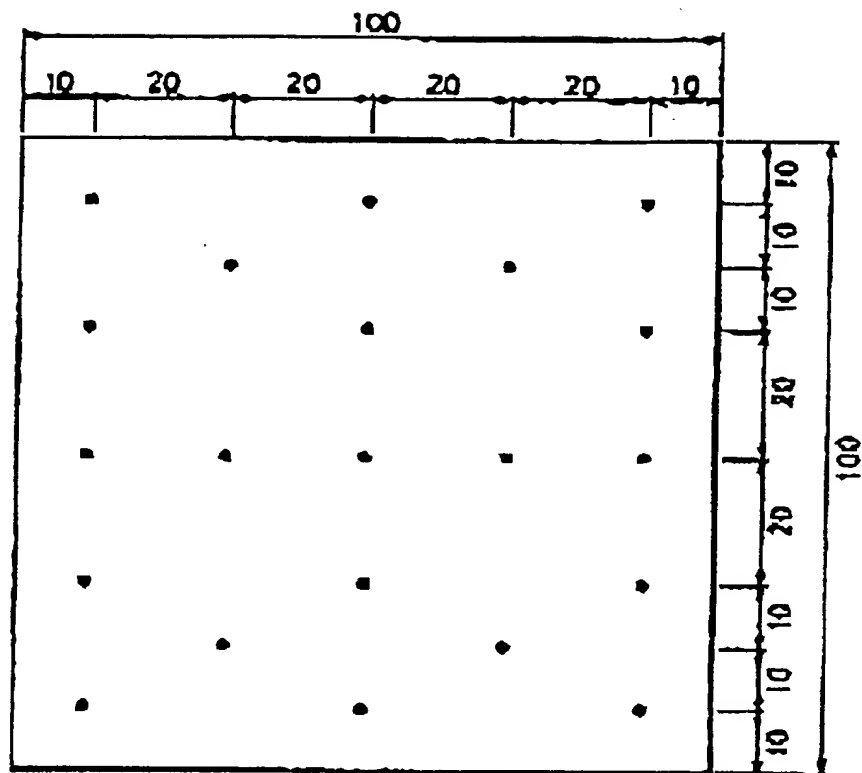
As described above, use of silicon nitride powders B, E and T with increased surface acidic group amount per surface area of the present invention remarkably improves the dispersibility in a mixing solvent and gives highly dense and uniform formed bodies and accordingly silicon nitride-based sintered bodies which are high in strength, small in the dispersion of strength and size and high in reliability can be easily obtained.

[0039]

Also, use of silicon nitride powders with increased ratio  $[Si^*/Si]$  of silicon  $[Si^*]$  derived from  $SiO_2$  to the surface silicon  $[Si]$  obtained by XPS in addition to the increased surface acidic group amount per B.E.T. surface area makes it possible to use water as a solvent and, therefore, highly dense and uniform formed bodies can be produced. Accordingly, silicon nitride-based sintered bodies with excellent characteristics can be economically obtained.

[Brief Description of the Drawings]

Fig. 1 illustrates density measurement points in a formed body.



• Mark: measurement point (n=21)

Size unit: mm

[Amendment]

3. The silicon nitride powder according to Claim 1, wherein the atomic ratio  $[Si^*/Si]$  of silicon  $[Si^*]$  derived from  $SiO_2$  to the surface silicon  $[Si]$  obtained by x-ray photospectrometry (XPS) is 0.07 or more.

文献4

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(54)【発明の名称】 窒化ケイ素粉末

(57)【要約】

【目的】 高強度で強度ばらつき、寸法ばらつきの小さい信頼性の高い窒化ケイ素焼結体を得ることができる窒化ケイ素粉末を提供する。

【構成】 窒化ケイ素粉末をB. E. T. 表面積当りの表面酸性基量が  $0.2\mu\text{eq}/\text{m}^2$  以上とすることにより、混合溶媒中での分散性が飛躍的に向上し、これを用いることにより高密度かつ均質な成形体を得ることができ、高強度で強度ばらつき、寸法ばらつきの小さい信頼性の高い窒化ケイ素焼結体を安易に作製することができる。

## 【特許請求の範囲】

【請求項1】 B、E、T、表面積当りの表面酸性基量が  $0.2\mu\text{eq}/\text{m}^2$  以上であることを特徴とする窒化ケイ素粉末。

【請求項2】 平均一次粒子径が  $0.5\mu\text{m}$  以下でB、E、T、表面積当りの表面酸性基量が  $1.0\mu\text{eq}/\text{m}^2$  以上であることを特徴とする請求項1記載の窒化ケイ素粉末。

【請求項3】 X線光電子分光〔XPS〕より求められる表面ケイ素〔Si〕のうち、 $\text{SiO}_2$ に帰属されるケイ素〔 $\text{Si}^*$ 〕の割合が原子比〔 $\text{Si}^*/\text{Si}$ 〕で0.01以上であることを特徴とする請求項1記載の窒化ケイ素粉末。

【請求項4】 X線光電子分光〔XPS〕より求められる表面ケイ素〔Si〕のうち、 $\text{SiO}_2$ に帰属されるケイ素〔 $\text{Si}^*$ 〕の割合が原子比〔 $\text{Si}^*/\text{Si}$ 〕で0.07以上であることを特徴とする請求項2記載の窒化ケイ素粉末。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、窒化ケイ素粉末、更に詳しくは、高強度で強度ばらつき、寸法ばらつきの小さい信頼性の高い窒化ケイ素焼結体を得るのに必要となる高密度かつ粉末の充填が均質な成形体を与える窒化ケイ素粉末に関する。

## 【0002】

【従来の技術】窒化ケイ素焼結体は、通常、窒化ケイ素粉末と主に $\text{Y}_2\text{O}_3$ 、 $\text{Al}_2\text{O}_3$ 等の焼結助剤粉末とをトリクロルエタン等の溶媒中でボールミル等により混合してスラリー化し、これに成形用バインダーを添加混合した後、直接、鑄込みや加圧鑄込み法により成形するか、もしくは、スラリーを乾燥してプレス成形あるいは射出成形により成形体を作り、この成形体を必要に応じて脱脂し、焼いて焼成して作製される。

【0003】これらの方法において、焼結助剤の種類、添加量および焼結条件が同じであれば、焼結体の物性、例えば強度や寸法精度および該物性のばらつきは、主に成形体の密度や充填構造により影響を受ける。従来、成形体の密度を増加させるために、原料となる窒化ケイ素粉末に関して、例えば特開平3-159907に示されるように粒径や粒度分布の制御が行われてきた。しかし、一方で焼結体物性向上の点から原料に用いられる窒化ケイ素粉末は微粒化される傾向にある（例えば、島村常夫ら、粉末と工業、P36、VOL.21、No. 8（1989）。）

## 【0004】

【発明が解決しようとする課題】ところが、微粒な窒化ケイ素粉末を原料に用いた場合、得られる成形体の密度が低く、成形体内部の密度斑やボアあるいは巣が発生するという問題があった。

【0005】そこで、本発明者らは、上記の問題点に鑑み鋭意検討した結果、窒化ケイ素粉末の表面特性によ

り、混合工程における窒化ケイ素粉末の溶媒中での分散性が大きく変化し、窒化ケイ素粉末の混合溶媒中での分散状態が成形体の粉末充填構造に影響を与えることを見出し本発明に至った。

【0006】従って本発明は、高密度で粉末の充填が均質な成形体を与えることができ、高強度で強度ばらつき、寸法ばらつきの小さい信頼性の高い窒化ケイ素焼結体を形成することができる窒化ケイ素粉末を提供することを目的としている。

## 【0007】

【課題を解決するための手段】すなわち、本発明はB、E、T、表面積当りの表面酸性基量が  $0.2\mu\text{eq}/\text{m}^2$  以上であることを特徴とする窒化ケイ素粉末である。

【0008】本発明におけるB、E、T、表面積当りの表面酸性基量が  $0.2\mu\text{eq}/\text{m}^2$  以上、好ましくは  $0.5\mu\text{eq}/\text{m}^2$  以上の窒化ケイ素粉末を用いることにより溶媒中での分散性が大幅に向上し、均質かつ高密度な成形体を得られる。一方、B、E、T、表面積当りの表面酸性基量が  $0.2\mu\text{eq}/\text{m}^2$  未満の窒化ケイ素粉末は、溶媒中での分散状態が著しく悪化し凝集が顕著となる。

【0009】さらに、焼結体の微細組織を制御するためには、平均一次粒子径  $0.5\mu\text{m}$  以下の微細な窒化ケイ素粉末を用いることが望ましい。このような微細粉末の場合、粉末間の凝集力が大きいため、溶媒中で十分に分散させるためには、B、E、T、表面積当りの表面酸性基量が  $1.0\mu\text{eq}/\text{m}^2$  以上であることが好ましい。

【0010】混合溶媒としては特に限定されないが、窒化ケイ素粉末のB、E、T、表面積当りの表面酸性基量を上記範囲に制御することによって、アルコール、水等の極性溶媒への分散性が著しく改善され、溶媒の誘電率が大きくなる程、この傾向は顕著となる。

【0011】溶媒として水は誘電率が大きくかつ安価で、可燃性有機溶媒のように防爆等の安全対策を必要としないため工業上非常に優れるが、窒化ケイ素の水に対する安定性が問題となる。これに対しては、X線光電子分光〔XPS〕より求められる表面ケイ素〔Si〕のうち $\text{SiO}_2$ に帰属されるケイ素〔 $\text{Si}^*$ 〕の割合が原子比〔 $\text{Si}^*/\text{Si}$ 〕で0.07以上の窒化ケイ素粉末を用いることにより、水中で安定して混合することができ、さらにB、E、T、表面積当りの表面酸性基量を上記範囲に制御することで分散性を高めることができる。該〔 $\text{Si}^*/\text{Si}$ 〕比が0.07未満の窒化ケイ素粉末を用いた場合、水によって窒化ケイ素が分解されるので好ましくない。

【0012】本発明におけるB、E、T、表面積当りの表面酸性基量を  $0.2\mu\text{eq}/\text{m}^2$  以上の窒化ケイ素粉末は、イミド分解法、直接窒化法等の方法で合成された窒化ケイ素粉末を1体積%以上の酸素を含む雰囲気あるいは0.5体積%以上の水蒸気雰囲気下で加熱処理することによって得ることができる。処理温度は酸素雰囲気の場合500～850℃、水蒸気雰囲気の場合は200～800℃が

好ましい。

【0013】上記熱処理により窒化ケイ素表面には $\text{SiO}_2$ 被膜が形成されるため、処理時間を制御することによって、窒化ケイ素表面の $[\text{Si}^+/\text{Si}]$ 比を0.07以上にすることができる。

【0014】窒化ケイ素粉末と焼結助剤粉末とを混合する際、各種溶媒を用いた湿式混合が一般に行われている。この際、主に、焼結助剤粉末の分散性を向上させるために界面活性剤や解膠剤が添加される。しかし、焼結助剤粉末の溶媒に対する分散性をいくら向上させたとしても、主成分である窒化ケイ素粉末の溶媒中での分散性が不十分であれば、窒化ケイ素粉末の凝集が生じ、特に10 鑄込み成形や加圧鑄込成形のような湿式成形においては、該窒化ケイ素粉末の凝集が成形体の密度斑やボアや巣の原因となる。

【0015】また、スプレードライヤー等による乾燥・造粒を行った場合にも造粒中にボアや粉末の不均一構造が生じる。さらに上記湿式成形や乾燥において、粉末間の凝集力が大きい程、脱溶媒に伴う粉末の接触が不均一となり疎な充填構造となり易く、不均質で低密度な成形体となってしまふ。

【0016】溶媒中において窒化ケイ素粉末に攪拌等により剪断力を与えると、弱い凝集体は一時的に解膠されるが、すぐに再凝集が生じるため、解膠、凝集の平衡状態により分散性が決まる。

【0017】極性溶媒においては、粉末表面電荷に起因する静電反発力がこの再凝集を抑制することで分散性に寄与しており、この静電反発力を有効に発現させるためには、先ず窒化ケイ素粉末粒子表面が溶媒で覆われることが必要条件となる。すなわち窒化ケイ素粉末とこれら\*30

$$\text{B. E. T. 表面積当りの表面酸性基量 } (\mu\text{eq}/\text{m}^2) = \frac{100/25 (\text{B}-\text{X}) \cdot \text{K}}{\text{W} \cdot \text{S}} \times 1000$$

W・S

X: HCl 水溶液の滴定量 (ml)

B: 空試験の滴定量 (ml)

K: HCl 水溶液の規定度 (N)

W: 窒化ケイ素粉末の重量 (g)

S: 窒化ケイ素粉末のB. E. T. 表面積 ( $\text{m}^2/\text{g}$ )

【0023】 $[\text{Si}^+/\text{Si}]$ 比 窒化ケイ素粉末を110℃で12時間真空乾燥した後、XPSの予備チャンバーで、室温、 $10^{-4} \sim 10^{-1}$  torrの真空中で1~8時間脱ガス処理を行い、分析チャンバーに試料を導入後、バックグラウンドの真空が $10^{-10}$  torr オーダーになってから測定を行った。表面のトータルケイ素 $[\text{Si}]$ は $\text{Si}_{2p}$ ピークより求め、さらに $\text{Si}_{2p}$ の波形分離を行い、 $103.4\text{eV} \pm 0.5\text{eV}$ のピークを $\text{SiO}_2$ に帰属されるケイ素 $[\text{Si}^+]$ として $[\text{Si}^+/\text{Si}]$ 比を原子比で求めた。測定にはPerkin Elmer社 ESCA5400MC を用いX線源は単色化したAl K $\alpha$ を用いた。

\* 溶媒との濡れ性が悪いと窒化ケイ素粉末の分散性が悪く、しかも溶媒に浸漬する以前に凝集しているものへは、凝集体を形成している粉末粒子間に溶媒が浸透せず、剪断力を与えても容易に解膠することが困難となると考えられる。

【0018】これに対して本発明による窒化ケイ素粉末は、極性溶媒との親和力が強い表面酸性基量を粉末表面全体を溶媒で濡らすのに必要な量存在させているため、溶媒との濡れ性が飛躍的に向上し、溶媒中での分散性を著しく改善することができる。

【0019】また、極性溶媒に水を用いた場合には、窒化ケイ素の水による分解が生じるが、本発明における上記 $[\text{Si}^+/\text{Si}]$ 比が0.07以上の窒化ケイ素粉末を用いた場合、窒化ケイ素粉末の表面に存在する $\text{SiO}_2$ 被膜により水による分解を防止することができる。

【0020】尚、本発明におけるB. E. T. 表面積当りの表面酸性基量および $[\text{Si}^+/\text{Si}]$ 比は以下の方法で求めた。

【0021】(B. E. T. 表面積当りの表面酸性基量) 窒化ケイ素粉末を110℃で12時間真空乾燥した後、10gを秤量し、これをポリプロピレン製フラスコに写し、1/100 規定NaOH水溶液を100ml 加えて、25℃で4時間振とうした。これを遠心分離により、粉末を沈降させ、上澄み液を25ml秤量し、フェノールフタレインを指示薬として1/100 規定HCl 水溶液で滴定した。同様に窒化ケイ素粉末を加えない系で空試験を行い、空試験の滴定値を規準として次式によりB. E. T. 表面積当りの酸性基量を求めた。尚、各試料について5回測定を行いその平均を測定値とした。

【0022】

【0024】以下、本発明の実施例について述べるが、本発明はこれに限定されるものではない。

【0025】

【実施例1】 $\alpha$ 結晶化率96.0%、平均一次粒子径0.2 $\mu\text{m}$ の窒化ケイ素粉末を10体積%の水蒸気を含むN<sub>2</sub>雰囲気または大気中で熱処理を行い表1に示す性状を有する窒化ケイ素粉末を作製した。

【0026】次にこれらの窒化ケイ素粉末92重量部に焼結助剤として平均一次粒子径0.25 $\mu\text{m}$ の $\text{Y}_2\text{O}_3$  5重量部と平均一次粒子径0.15 $\mu\text{m}$ の $\text{Al}_2\text{O}_3$  3重量部を添加し、粉末総量に対して70重量%のエタノールを加えナイロン製ボールミルにより100rpmで48時間混合した後、バインダーを粉末総量に対して0.5重量%添加し、続いて1時間混合した。得られたスラリーを真空脱泡後、多孔型へ30kg/cm<sup>2</sup>の圧力で加圧鑄込成形を行い10cm×10cm×5.5mmの成形体を得た。この成形体を100℃で12時間乾燥

後、図1に示した個所の密度を $\gamma$ 線微小部密度測定装置により測定した。測定結果および成形前のスラリーの粘度を表2に示す。また、成形体の重量および寸法より算出したバルク密度も同表に示す。

【0027】乾燥後の成形体を切断、研削により $8\text{mm} \times 48\text{mm} \times 5.5\text{mm}$ の試験片16本に加工した。この試験片を $750^\circ\text{C}$ で3時間脱脂し、 $\text{N}_2$ 雰囲気下、 $1720^\circ\text{C}$ で5時間焼成した後、 $1720^\circ\text{C}$ 、 $1000$ 気圧の $\text{N}_2$ 中で3時間HIP処理した。

【0028】得られた焼結体の密度をアルキメデス法により求め、厚みを測定した後、JISR1601に準拠した抗折試験片に加工し四点曲げ試験を行った。結果を表2に示す。

【0029】表2の結果より、比較例(A, B)に対して本発明の窒化ケイ素粉末(C~I)を用いた場合、エタノール中での分散性向上に伴うスラリーの粘度の低下が認められ、高密度で密度ばらつきの小さな成形体得られる。焼結体の平均強度、ワイブル係数、寸法精度が大幅に向上することがわかる。

【0030】

【実施例2】表1の窒化ケイ素粉末A~Iについて、溶媒に水を用いて下記手順で実施例1と同様の成形体を作製した。

【0031】窒化ケイ素粉末92重量部、実施例1で用いた $\text{Y}_2\text{O}_3$  5重量部および $\text{Al}_2\text{O}_3$  3重量部を準備し、先ず窒化ケイ素粉末にアンモニアでpH 9.5に調整したイオン交換水

10

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表

\* 換水を粉末総量に対して48重量%加え、ナイロン製ボールミルにより100rpmで12時間混合し、続いてこれに $\text{Y}_2\text{O}_3$ 、 $\text{Al}_2\text{O}_3$ を添加して12時間混合した後、粉末総量に対して0.5重量%のバインダーを加えて、さらに1時間混合した。得られたスラリーのpHを測定したところ、窒化ケイ素粉末A, B, E及びGのスラリーは各々pH 11.2, pH 10.7, pH 11.0, pH 10.8にpH値が増加しており、水による窒化ケイ素粉末の分解が生じていることが認められた。

【0032】このスラリーの真空脱泡後、実施例1と同様に成形体、焼結体を作製し、それらの成形体および焼結体の特性を測定した。結果を表3に示す。

【0033】表3より、実施例1の結果(表2)と同様に比較例(A, B)に対して本発明の窒化ケイ素粉末(C~I)を用いた場合、高密度から密度ばらつきの小さい成形体得られ、焼結体特性も向上することがわかる。

【0034】また、 $[\text{Si}^+/\text{Si}]$ 比が0.07未満の窒化ケイ素粉末A, B, E, Gにおいては、水による分解が生じ、溶媒にエタノールを用いた場合(表2)に比べて成形体および焼結体特性が低下しているが、 $[\text{Si}^+/\text{Si}]$ 比が0.07以上のC, D, F, H, Iにおいては、水による分解もなく、エタノール溶媒に比べさらに成形体および焼結体の特性が向上した。

【0035】

【表1】

1

窒化ケイ素粉末 No.	比較例		本 発 明						
	A	B	C	D	E	F	G	H	I
B, E, T. 表面積当りの表面酸性基量 ( $\mu\text{eq}/\text{m}^2$ )	0.03	0.15	0.23	0.62	0.65	1.20	1.23	2.14	2.51
$[\text{Si}^+/\text{Si}]$ 比 (原子比)	0.04	0.05	0.07	0.11	0.04	0.20	0.05	0.18	0.17

【0036】

【表2】

【0037】

表 2

窒化ケイ素粉末 No.			比較例		本 発 明						
			A	B	C	D	E	F	G	H	I
スラリー粘度 (CP)			2650	2400	1330	1000	1030	620	618	585	540
成形体 密度 (g/cm <sup>3</sup> )	γ線微小	平均密度	1.581	1.586	1.620	1.635	1.633	1.668	1.670	1.675	1.679
	部密度	ばらつき巾	0.035	0.033	0.017	0.016	0.017	0.010	0.009	0.007	0.007
	バルク体	密度	1.582	1.585	1.620	1.634	1.634	1.668	1.669	1.675	1.678
焼結体 特性	厚み寸法 (mm)	平均厚み	4.320	4.323	4.359	4.368	4.367	4.401	4.400	4.406	4.410
		ばらつき巾	0.125	0.118	0.059	0.053	0.054	0.028	0.030	0.025	0.024
	強度	抗折強度 (kg/mm <sup>2</sup> )	105	107	115	117	116	122	122	124	123
ワイヤル係数			13	14	18	19	18	21	21	22	22

【表3】



表 3

窒化ケイ素粉末 No.			比較例		本 発 明						
					A	B	C	D	E	F	G
スラリー	粘度 (C P)		5500	4950	2850	2300	2890	1050	2030	250	230
	p H		11.2	10.7	9.7	9.6	11.0	9.5	10.8	9.5	9.5
成形体 密度 (g/cm³)	γ線微小 部密度	平均密度	1.583	1.585	1.698	1.720	1.705	1.807	1.769	1.842	1.850
		ばらつき	0.042	0.035	0.014	0.012	0.020	0.009	0.022	0.006	0.007
	バルク体	密度	1.584	1.592	1.696	1.721	1.705	1.808	1.769	1.853	1.856
		平均厚み	4.322	4.322	4.428	4.462	4.430	4.521	4.490	4.554	4.554
焼結体 特性	厚み寸法 (mm)		0.134	0.124	0.033	0.031	0.062	0.015	0.058	0.012	0.012
	強度	抗折強度 (kg/mm²)	98	100	120	123	112	126	115	129	128
		ワイプル係数	12	12	20	20	17	24	18	25	26

【0038】

【発明の効果】以上述べたように、本発明のB、E、T、表面積当りの表面酸性基量を増加させた窒化ケイ素粉末を用いることにより、混合溶媒中での分散性が飛躍的に向上し、高密度かつ均質な成形体を得ることができ、高強度で強度ばらつき、寸法ばらつきの小さい信頼性の高い窒化ケイ素焼結体を容易に作製することができる。

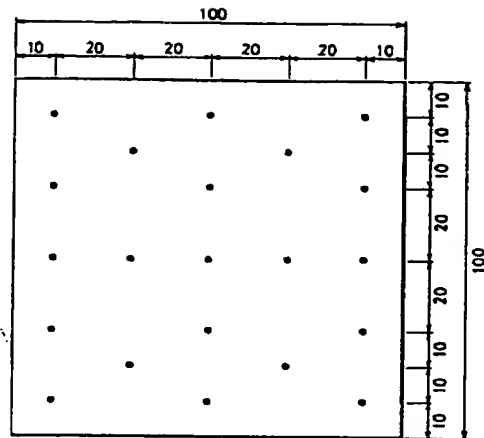
【0039】また、B、E、T、表面積当りの表面酸性

基量の増加に加えXPSより求められる表面ケイ素[Si]のうち、SiO<sub>2</sub>に帰属されるケイ素[Si<sup>+</sup>]の割合[Si<sup>+</sup>/Si]比を増加させた窒化ケイ素粉末を用いることにより、水を溶媒に使用できるため、さらに高密度かつ均質な成形体を作製でき、さらに特性の優れた窒化ケイ素焼結体を安価に得ることができる。

【図面の簡単な説明】

【図1】成形体の密度測定個所の説明図。

【図1】



●印：測定点（ $n=21$ ）

寸法単位：mm

【手続補正書】

【提出日】平成4年10月14日

【手続補正1】

【補正対象書類名】明細書

【補正対象項目名】請求項3

【補正方法】変更

【補正内容】

【請求項3】 X線光電子分光〔XPS〕より求められる表面ケイ素〔Si〕のうち、 $\text{SiO}_2$ に帰属されるケイ素〔 $\text{Si}^*$ 〕の割合が原子比〔 $\text{Si}^*/\text{Si}$ 〕で0.07以上であることを特徴とする請求項1記載の窒化ケイ素粉末。